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(54) Title: METHODS FOR CLEANING MICROELECTRONIC STRUCTURES

(57) Abstract: A method of cleaning and removing water, entrained solutes and particulate matter during a manufacturing process from a microelectronic device comprises the steps of: (a) providing a partially fabricated integrated circuit, MEM's device, or optoelectronic device having water and entrained solutes on the substrate; (b) providing a densified carbon dioxide cleaning composition, the cleaning composition comprising carbon dioxide and, optionally but preferably, a cleaning adjunct; (c) immersing the surface portion in the densified carbon dioxide drying composition; and then (d) removing the cleaning composition from the surface portion.

METHODS FOR CLEANING MICROELECTRONIC STRUCTURES

Field of the Invention

The present invention concerns methods and apparatus for removing water and aqueous-borne solutes from substrates such as semiconductor substrates, MEM's, or optoelectronic devices with liquid or supercritical carbon dioxide

Background of the Invention

Production of integrated circuits, microelectronic devices, and micro-electro mechanical devices, (MEM's) involve multiple processing steps many of which incorporate water as either a carrier of chemistry, or a media to facilitate the removal of process byproducts. The evolution of materials and processes has been lead by a drive toward smaller feature sizes and more complex microdevices. In some cases, the use of water in these evolving processes has resulted in challenges whereby deleterious effects of water and byproducts carried by water have been seen. The unique physical properties of dense carbon dioxide in a liquid or supercritical state are of particular interest in preventing certain of these pitfalls.

One such process where dense CO_2 is of practical application relates to prevention of surface tension or capillary force induced image collapse. This is of particular interest during the aqueous development of micro-lithographic images using photoresists. Photoresists are photosensitive films used for transfer of images to a substrate. A coating layer of a photoresist is formed on a substrate and the photoresist layer is then exposed, through a photomask or by other techniques, to a source of activating radiation. Exposure to activating radiation provides a photoinduced chemical transformation of the photoresist coating to thereby transfer the pattern of the photomask (or other pattern generator) to the photoresist coated substrate. Following exposure, the photoresist is developed to provide a relief image that permits selective processing of a substrate. *See. e.g.*, U.S. Patent No. 6,042,997.

A photoresist can be either positive-acting or negative-acting. For negative acting resists, the solubility of the exposed region is decreased such that it remains on the wafer during development while the non-exposed region is removed. For positive acting resists the solubility of the exposed region increases in the developer solution, so it is removed during the development step leaving the unexposed region unaffected. Positive and negative acting resist materials typically incorporate chemical functionality that undergoes a transformation upon exposure to UV light at a given wavelength. The transformation is often referred to as a "polarity switch" because polymer polarity increases or decreases are often the driving force for changes in the solubility of the polymer in the developing solution. This transformation is facilitated by the incorporation of photoacid generators (PAG's) or photobase generators (PGB's) into the resist compositions. The acid and base moieties are typically generated upon exposure to the appropriate source of radiation followed by heat. The developer solutions are typically aqueous, and are typically dried from the substrate before further processing.

Capillary forces present in the aqueous drying of imaged resist patterns can result in resist deformation and pattern collapse. This problem becomes particularly serious as lithography techniques move toward smaller image nodes with larger aspect ratios. Researchers have suggested that collapse problems associated with aqueous drying will affect the 130-nm technology node, and will become more prevalent in subsequent technologies as aspect ratios increase.

Researchers at both IBM and NTT have suggested that the use of carbon dioxide in supercritical resist drying (SRD) may reduce image collapse and film damage. *See, e.g.*, H. Namatsu, *J. Vac. Sci. Technol. B* **18(6)**, 3308-3312 (2000); D. Goldfarb et al., *J. Vac. Sci. Technol B.* **18(6)** 3313-3317 (2000). However, while the absence of surface tension and the accessible critical temperature and pressure of CO_2 have been touted as positives factors for this drying approach, the relatively low solubility of water in the supercritical phase has also been described as a challenge that may necessitate the use of chemical adjuncts to increase the transport capacity of the fluid. Researchers at IBM and NTT have demonstrated the use of certain surfactants in supercritical fluid-aided drying. However, the surfactant is described as being incorporated into a hexane pre-rinse in "indirect SRD" *See, e.g.*, Goldfarb et al.,

supra, or only particular surfactants have been incorporated into the carbon dioxide in "direct SRD". In both the direct and indirect drying methods the choice of surfactants and co-solvents is limited by what is described as compatibility issues leading to resist damage. Accordingly, there remains a need for new approaches to SRD using carbon dioxide.

Another problem with drying of surfaces on microelectronic substrates (e.g. photoresist coated semiconductor wafers, MEMS, opto-electronic devices, photonic devices, flat panel displays, etc) is the complete removal of aqueous processing, cleaning or rinsing solutions without leaving a residue, commonly referred to as a drying watermark. These watermarks result from the concentration of solutes in the aqueous processing, cleaning, or drying fluid, as said fluid is dried. In many microelectronic, optical, micro-optical, or MEMS structures this watermark can negatively impact the manufacturing yield or ultimate performance of the device. There needs to be an effective method to remove (clean) water-based fluids from surfaces that eliminates the concentration and ultimate deposition of entrained solutes – eliminating watermarks.

One such challenge comes in the manufacturing of MEM's devices. Wet-processing steps generally culminate with a rinse and dry step. Evaporative drying causes water with low levels of solutes that is pooled on the surface and in various micro-features to concentrate in locations that maximize the surface area of the pool. As a result, these drying steps can lead to the concentration of once dissolved solutes in close proximity to or on motive parts. The deposited materials which can be organic or inorganic in nature contribute to stiction, the locking of the motive part such that it cannot be actuated. "Release stiction" as it is termed during the manufacturing step results, is believed to be derived from adhesive and Van der Waals forces and friction. The forces generated by this phenomenon can completely incapacitate motive parts on MEM's devices.

To combat stiction manufacturers of MEM's devices use solvents such as small chain alcohols that reduce surface tension during the rinse step and facilitate a more even drying process. However, these steps alone have not eliminated the occurrence of stiction. Supercritical CO_2 has been proposed for drying microstructures, (see Gregory T. Mulhern "Supercritical Carbon Dioxide Drying of

Micro Structures") where surface tension forces can cause damage. Researchers at Texas Instruments Inc. among others (*see, e.g.,* U.S. Patent No. 6,024,801) have demonstrated that supercritical CO_2 can be used to clean organic and inorganic contaminants from MEM's devices prior to a pacification step, thus limiting stiction.

These technologies utilizing supercritical CO_2 do not limit stiction by combination of drying and cleaning where water and solutes are removed simultaneously so to avoid the concentration of water and solutes at specific site. Technologies are needed that can prevent release stiction through an integrated process of drying, cleaning, and surface pacification.

Other examples of drying and cleaning challenges related to aqueous wet-processing steps come in the formation of deep vias for interlayer metalization in the production of integrated circuits. These vias, formed by methods known to those familiar with the art, typically have large critical aspect ratios creating geometries that can be difficult to clean residues from. Furthermore, wet-processing steps and rinses with traditional fluids such as water leave once dissolved solutes behind upon evaporative drying. These solutes deposited at the bottom of the vias can inhibit conduction upon metalization lowering functional yields.

Technologies are needed that remove water (dry) and dissolved solutes (clean) from vias after wet processing steps, thus reducing yield losses.

Summary of the Invention

A first aspect of the present invention is a method of cleaning a microelectronic device, comprising the steps of: providing a substrate having a surface portion to be cleaned, providing a densified carbon dioxide cleaning composition, the composition comprising carbon dioxide and a cleaning adjunct, the cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof; immersing the surface portion in the densified carbon dioxide composition; and then removing said cleaning composition from the surface portion; while maintaining the cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step. Examples of devices that may be cleaned by the present invention include, but are not limited to,

microelectromechanical devices (MEMs), optoelectronic devices, and resist-coated substrates.

In a particular embodiment the present invention provides a method for removing water and entrained solutes from a microelectronic device such as resist-coated substrate (such as a semiconductor substrate), a MEMs device, or an opto-electronic device is disclosed herein. In such a method, the cleaning/removal of the water may also be referred to as "drying" of the water from the device. In general, the method comprises the steps of: *(a)* providing a substrate having a an imaged or patterned feature such as a resist coated silicon wafer and having water on the resist coating; *(b)* providing a densified (e.g., liquid or supercritical) carbon dioxide drying composition, the drying composition comprising carbon dioxide and a drying adjunct, the drying adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof; *(c)* immersing the surface portion in the densified carbon dioxide drying composition; and then *(d)* removing the drying composition from the surface portion.

Various particular embodiments of the invention are discussed further below.

Cyclic phase modulation. A further aspect of the present invention is a method of cleaning a microelectronic device, to remove soluble material, particulate matter, and/or contaminants, etc. The method comprises the steps of: providing a substrate having a surface portion to be cleaned, providing a densified carbon dioxide cleaning composition, the composition comprising carbon dioxide and, optionally but preferably a cleaning adjunct, the cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof; immersing the surface portion in the densified carbon dioxide composition to thereby clean the surface portion; and then removing said cleaning composition from the surface portion. The immersing/cleaning step described above is preferably carried out with cyclical phase modulation, as explained in greater detail below, during some or all of that step.

Aqueous cleaning systems. A further aspect of the present invention is a method of cleaning a microelectronic device, comprising the steps of: providing a substrate having a surface portion to be cleaned, providing a densified carbon dioxide cleaning composition, the composition comprising carbon dioxide and water. Optionally, but preferably, one or more cleaning adjuncts are included in the cleaning

composition, in an amount sufficient to facilitate cleaning of the article to be cleaned. Suitable cleaning adjuncts include, for example, cosolvents, surfactants, water-soluble cleaning adjuncts, and combinations thereof. The next steps of the method comprise immersing the surface portion in the densified carbon dioxide cleaning composition to thereby clean the article, and then removing said cleaning composition from the surface portion.

Particulate cleaning. A further aspect of the present invention is a method of cleaning/removing solid particulates from a microelectronic device, the method comprising the steps of: providing a substrate having a surface portion to be cleaned, providing a densified carbon dioxide cleaning composition, the composition comprising carbon dioxide and, optionally but preferably a cleaning adjunct, the cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof; immersing the surface portion in the densified carbon dioxide composition for a time sufficient to remove solid particulate contaminants therefrom; and then removing said cleaning composition from the surface portion. Particulate contamination of a substrate may be found, for example, following chemical-mechanical planarization of a substrate.

Control of contaminant redeposition. In one preferred embodiment, process parameters are preferably controlled so that the drying and cleaning composition is maintained as a homogeneous composition during the immersing step, the removing step, or both the immersing and removing step, without substantial deposition of the drying adjunct or the aqueous entrained solutes on the resist coating, the patterned feature, or the mechanical, electrical, or optical components of the device or circuit.

The present invention is explained in greater detail in the drawings and specification set forth below.

Brief Description of the Drawings

Figure 1 shows a substrate having a patterned resist layer formed thereon, with water present in various locations thereon.

Figure 2 schematically illustrates an apparatus for carrying out the methods of the present invention.

Figure 3 depicts a phase diagram of predominantly CO_2 system representing the plausability of a transition from a predominantly CO_2 supercritical mixture to a gas avoiding a liquid phase.

Figure 4 schematically illustrates an apparatus for carrying out the methods of the present invention.

Figure 5 schematically illustrates another embodiment of an apparatus for carrying out the methods of the present invention.

Detailed Description of the Preferred Embodiments

Examples of devices that may be cleaned by the present invention include, but are not limited to, microelectromechanical devices (MEMs), optoelectronic devices, and resist-coated substrates. The resist typically comprises a polymeric material, and may be a positive-acting resist or a negative-acting resist. The resist may be patterned or unpatterned, developed or undeveloped at the time the drying process is carried out.

Any suitable resist composition can be used to carry out the present invention, including but not limited to those described in U.S. Patents Nos. 6,042,997; 5,866,304; 5,492,793; 5,443,690; 5,071,730; 4,980,264; and 4,491,628. Applicants specifically intend that the disclosures of all United States patent references that are cited herein be incorporated herein by reference in their entirety.

The resist compositions may be applied to the substrate as a liquid compositions in accordance with generally known procedures, such as by spinning, dipping, roller coating or other conventional coating technique. When spin coating, the solids content of the coating solution can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning.

The resist compositions are suitably applied to substrates conventionally used in processes involving coating with photoresists. For example, the composition may be applied over silicon wafers (that may include one or more layers thereon such as silicon dioxide, silicon nitride, polysiloxand and/or metal, etc.) for the production of microprocessors and other integrated circuit components. Aluminum-aluminum oxide, gallium arsenide, ceramic, quartz or copper substrates also may be employed.

Substrates used for liquid crystal display and other flat panel display applications are also suitably employed, e.g. glass substrates, indium tin oxide coated substrates and the like.

Following coating of the photoresist onto a surface, it is dried by heating to remove the solvent until preferably the photoresist coating is tack free. Alternatively it may be dried by the procedures described herein. Thereafter, it is imaged in a conventional manner. The exposure is sufficient to effectively activate the photoactive component of the photoresist system to produce a patterned image in the resist coating layer.

Following exposure, the film layer of the composition may be baked. Thereafter, the film is developed by contacting the film resist layer to any suitable developer solution (the choice of which will depend in part upon the particular choice of resist material). For example, the developer may be a polar developer, for example an aqueous based developer such as an inorganic alkali exemplified by sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, sodium silicate, sodium metasilicate; quaternary ammonium hydroxide solutions such as a tetra-alkyl ammonium hydroxide solution; various amine solutions such as ethyl amine, n-propyl amine, diethyl amine, di-n-propyl amine, triethyl amine, or methyldiethyl amine; alcohol amines such as diethanol amine or triethanol amine; cyclic amines such as pyrrole, pyridine, etc. In general, development is in accordance with art recognized procedures. After development the resist is optionally rinsed (for example with an aqueous rinse) and is then dried, preferably by the drying procedures described herein.

Following development of the photoresist coating over the substrate, the developed substrate may be selectively processed on those areas bared of resist, for example by chemically etching or depositing on substrate areas bared of resist in accordance with procedures known in the art. For the manufacture of microelectronic substrates, e.g., the manufacture of silicon dioxide wafers, suitable etchants include a gas etchant, e.g. a chlorine or fluorine-based etchant such a CF_4 or CF_4 /CHF_3 etchant applied as a plasma stream, in accordance with known techniques.

Carbon-dioxide cleaning drying compositions used to carry out the present invention typically comprise:

(a) carbon dioxide to balance, typically at least 20, 30, 40, 50 or 60 percent;

(b) from 0, 0.01, 0.1, 0.5, 1 or 2 percent to 5 or 10 percent or more of surfactant;

(c) from 0, 0.01, 0.1, 1 or 2 to 30, 40 or 50 percent or more of an organic co-solvent;

(d) optionally, but in some embodiments preferably, from 0, 0.01, or 0.1 to 2, 5 or 10 percent water; and

(e) when water is included a water-soluble compound/cleaning adjunct to be delivered is included in an amount sufficient to facilitate cleaning of the substrate.

Preferably at least one of the surfactant and/or the co-solvent is included (*e.g.*, by at least 0.01 percent) in the cleaning/drying composition, and optionally both a surfactant and a co-solvent may be included in the composition. Water may or may not be included in the composition, depending upon the particular cleaning application and the nature of the substrate. Percentages herein are expressed as percentages by weight unless otherwise indicated.

The cleaning/drying composition may be provided as a liquid or supercritical fluid, including cryogenic liquids. Liquid and supercritical carbon dioxide are herein together referred to as "densified" carbon dioxide in accordance with established usage.

The organic co-solvent may be one compound or a mixture of two or more ingredients The organic co-solvent may be or comprise an alcohol (including diols, triols, etc.), ether, amine, ketone, carbonate, or alkanes, or hydrocarbon (aliphatic or aromatic) The organic co-solvent may be a mixture of compounds, such as mixtures of alkanes as given above, or mixtures of one or more alkanes in combination with additional compounds such as one or more alcohols as described above. (e.g., from 0 or 0.1 to 5% of a C1 to C15 alcohol (including diols, triols, etc.)). Any surfactant can be used to carry out the present invention, including both surfactants that contain a CO_2 -philic group (such as described in PCT Application WO96/27704) linked to a CO_2 -phobic group (e.g., a lipophilic group) and surfactants that do not contain a CO_2 -philic group (i.e., surfactants that comprise a hydrophilic group linked to a hydrophobic (typically lipophilic) group). A single surfactant may be used, or a combination of surfactants may be used. Numerous surfactants are known to those

skilled in the art. See, e.g., McCutcheon's Volume 1: Emulsifiers & Detergents (1995 North American Edition) (MC Publishing Co., 175 Rock Road, Glen Rock, N.J. 07452). Examples of the major surfactant types that can be used to carry out the present invention include the: alcohols, alkanolamides, alkanolamines, alkylaryl sulfonates, alkylaryl sulfonic acids, alkylbenzenes, amine acetates, amine oxides, amines, sulfonated amines and amides, betaine derivatives, block polymers, carboxylated alcohol or alkylphenol ethoxylates, carboxylic acids and fatty acids, a diphenyl sulfonate derivatives, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and/or amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fluorocarbon-based surfactants, glycerol esters, glycol esters, hetocyclic-type products, imidazolines and imidazoline derivatives, isethionates, lanolin-based derivatives, lecithin and lecithin derivatives, lignin and lignin derivatives, maleic or succinic anhydrides, methyl esters, monoglycerides and derivatives, olefin sulfonates, phosphate esters, phosphorous organic derivatives, polyethylene glycols, polymeric (polysaccharides, acrylic acid, and acrylamide) surfactants, propoxylated and ethoxylated fatty acids alcohols or alkyl phenols, protein-based surfactants, quaternary surfactants, sarcosine derivatives, silicone-based surfactants, soaps, sorbitan derivatives, sucrose and glucose esters and derivatives, sulfates and sulfonates of oils and fatty acids, sulfates and sulfonates ethoxylated alkylphenols, sulfates of alcohols, sulfates of ethoxylated alcohols, sulfates of fatty esters, sulfonates of benzene, cumene, toluene and xylene, sulfonates of condensed naphthalenes, sulfonates of dodecyl and tridecylbenzenes, sulfonates of naphthalene and alkyl naphthalene, sulfonates of petroleum, sulfosuccinamates, sulfosuccinates and derivatives, taurates, thio and mercapto derivatives, tridecyl and dodecyl benzene sulfonic acids, etc.

Figure 1 illustrates a resist-coated substrate article **10** to be dried by the method of the present invention. The article comprises a substrate **11**, which may comprise silicon or any other suitable material as described above, and which may itself comprise one or more layers, having a resist coating **12** formed thereon. Water droplets **14, 15**, to be removed by drying, are on the top surface and in a trench formed in the resist coating.

Figure 2 schematically illustrates an apparatus for carrying out the method of the invention. The apparatus comprises an enclosed drying vessel **21**, suitable for containing liquid or supercritical carbon dioxide, in which vessel the coated substrate **10** (or other microelectronic device to be cleaned) is positioned on a suitable support **27**. The drying vessel may include a door, a stirring device or other means of agitation, a view window, a compressor connected to the drying vessel to increase or decrease the pressure therein, a heat exchanger, heater or cooler connected to the drying vessel to increase or decrease the temperature of the contents thereof, etc.

A carbon dioxide cleaning/drying composition supply **22** is connected to the drying vessel by appropriate piping. The cleaning/drying composition supply **22** may itself comprise one or more storage vessels, pumps, valves, piping for mixing the drying adjunct into the carbon dioxide, etc. The vessel may be filled with the cleaning/drying composition to a level **28** above the article to be cleaned **10.**

Depending upon the particular technique or combination of techniques being employed to control the processing conditions, the system includes a supply of a second gas, second material, and/or additional carbon dioxide **24** connected to the drying vessel **21.**

If desired, a developer solution supply **25** may be connected to the vessel so that both development and drying of the substrate may be carried out in the same vessel **21.**

A draining system **26** is preferably connected to the vessel **21** for draining whatever composition is contained therein. The draining system may itself comprise appropriate pumps, valves, compressors and the like (some of which components may be serve multiple functions in conjunction with supply elements described above), may include a still for distilling and optionally recycling ingredients such as carbon dioxide, and may include suitable piping, valves, etc. for recycling various compositions or constituents thereof to supply elements for re-use. For example, used drying composition may be distilled to allow carbon dioxide to be recycled and re-used as part of the drying composition, or to the source of additional carbon dioxide supply.

As noted above, the method of the invention comprises the steps of:

(a) providing a substrate having a an imaged or patterned feature such as a resist coated silicon wafer and having water on the resist coating;

(b) providing a densified (e.g., liquid or supercritical) carbon dioxide drying composition, the drying composition comprising carbon dioxide and a drying adjunct, the drying adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

(c) immersing the surface portion in the densified carbon dioxide drying composition; and then

(d) removing the drying composition from the surface portion.

The process parameters may be controlled so that the drying composition is maintained as a homogeneous composition during the immersing step, the removing step, or both the immersing and removing step, without substantial deposition or redeposition of the drying adjunct or contaminants on the resist coating.

Preferably, the providing step is carried out by mixing the carbon dioxide with the adjunct to produce a homogeneous solution, and then the immersing step is carried out while maintaining the drying composition as a homogeneous solution. Such mixing can be carried out in the drying composition supply 22 by any suitable means, such as stirring, injection under pressure, etc.

The removing step is preferably carried out while maintaining the drying composition as a homogeneous solution. In general, this is achieved by inhibiting the boiling of the drying composition as it is drained from the drying vessel. When draining liquid CO_2 from a vessel the liquid reaches a state where it is at equilibrium with CO_2 vapor, termed saturated vapor pressure. To maintain saturation, as liquid is removed from the vessel by venting or pumping preferably from the bottom of the vessel, the liquid phase boils to generate vapor for the increasing volume of the vapor phase. This boiling which may be nucleated at liquid/gas, and liquid/solid interfaces causes adjuncts with lower vapor pressure than CO_2 including, co-solvents and surfactants, and solute contaminants to concentrate at interfaces. Concentrated adjuncts, deposited contaminants and interfacial stresses created by boiling at liquid/solid interfaces can be damaging to resist features, MEM's, or other patterned microdevices. In the case of imaged and developed resists, feature sizes less 130-

nmwith aspect ratios greater than 3 are particularly susceptible to damage. Process controls to prevent such damage are as follows.

For example, when the drying composition is a liquid drying composition, the removing step may be carried out by pressurizing the enclosed chamber with a second compressed gas (*e.g.*, helium, nitrogen, air, mixtures thereof) from supply **24** by an amount sufficient to inhibit boiling of the drying composition during the draining step. The second gas is preferably one that is substantially immiscible in the drying composition possessing a saturated vapor pressure that is higher than CO_2. The second gas may be used to itself force the drying composition from the vessel, or the drying composition may be pumped or otherwise drained from the vessel while the second gas maintains an over-pressurization at the gas-liquid interface formed in the wash vessel during draining thereof.

Alternatively, if the drying composition is in the liquid phase, the draining step can be accomplished without boiling by liquid-gas equilibration with a secondary chamber or storage vessel. In this scenario, drying chamber **21** is connected to storage vessel **31** by gas-side line **32** (top), and liquid-side line **33**. Each line contains a valve **34, 35** to separate or isolate vessels **21** and **31** from one another. During the draining step, storage vessel **31** contains a liquid CO_2 composition at a saturated pressure equal to or in excess of the saturated vapor pressure in the cleaning/drying vessel **21**. Draining may be accomplished by first opening the gas-side connection **32** between vessels **21** and **31**, and then opening the liquid-side connection **33**. Liquid flows from cleaning vessel **21** to storage vessel **31** by gravity, if **21** is located sufficiently above **31**, amd/or by pumping. Liquid transfer described above avoids boiling thereby avoiding potential damage to resist features or other device features.

When the drying composition is a supercritical drying composition there will not be a gas-liquid interface. In this case, the removing step may be carried out by first adding a second material (*e.g.*, a cosolvent as described above or a secondary gas) to the supercritical drying composition so that it is converted to a liquid drying composition, which can then be removed from the vessel as described above. If a secondary gas is used to cause the supercritical fluid phase to change to a liquid, the gas should be chosen from those having a saturated vapor pressure that is higher than that of CO_2 and/or a critical pressure and temperature higher than that of CO_2.

Exemplary gases include but are not limited to: nitrogen, argon, helium, oxygen, and mixtures thereof.

Alternatively, when the drying composition is in the supercritical state, the adjunct containing fluid can be sufficiently diluted prior to the draining step by simultaneous addition of pure supercritical CO_2 and removal of adjunct-containing supercritical CO_2. After sufficient fluid turnover is accomplished and adjunct concentration is effectively minimized, the supercritical fluid is vented from the drying vessel by maintaining the fluid in the supercritical state until a transition is made directly to the gas state thus avoiding the liquid state. This is accomplished during the draining/venting step by maintaining the fluid temperature above the critical temperature of the mixture (Tc) until the pressure in the vessel is below the critical pressure of the mixture (Pc). **Figure 3** depicts a phase diagram of predominantly CO_2 system representing the plausibility of a transition from a predominantly CO_2 supercritical mixture to a gas avoiding a liquid phase. Because the expansion of the supercritical fluid and subsequent expansion of the remaining gas is an endothermic process, heat may need to be added to the system to maintain the temperature of the fluid or gas above the critical temperature thus avoiding condensation of the supercritical fluid or gas to a liquid or solid. By effecting a direct transition from the supercritical phase to the gas phase, liquid boiling is avoided thereby avoiding the interfacial stress caused by a retracting liquid meniscus at the liquid/solid interface, and unwanted deposition of solutes onto and in microstructures.

In another embodiment, the removing step is carried out by diluting the drying composition with additional carbon dioxide from supply **24**, during which dilution the drying composition is removed from the vessel by draining system **23**. Since larger quantities of carbon dioxide are required for such a technique, the use of a still to distill drained carbon dioxide, along with appropriate piping and valving for returning the carbon dioxide to supply **22** or supply **24** for subsequent re-use, is preferred.

In still another embodiment, a secondary gas is used, at a pressure range above the saturation point of CO_2 gas, to displace liquid and gaseous CO_2 in the drying chamber leaving a predominance of the secondary gas in the vapor phase. The secondary gas, possessing a lower heat of compression, can be vented from the chamber to ambient pressure with less heat loss to the system. Also represented by a

smaller Joule-Thomson coefficient, (μ), the expansion of the gas from high pressure to atmospheric conditions results in less change in temperature at or in close proximity to the substrate. ($\mu_{CO_2} > \mu_X$, where X = secondary gas).

$$\mu = (dT/dP)_H$$

In this embodiment, the secondary gas is useful in avoiding thermal shock when rapid cycling of pressure is desired for high throughput. Substrates such as silicon wafers can crack or become damage when significant temperature gradients exist in that substrate. Cooling of chambers and vessels from gaseous expansion can also add valuable processing time and require substantial heat input for temperature regulation. The use of a secondary gas can minimize heat loss and heat inputs, potentially reducing cycle time and energy requirements.

Cyclic phase modulation. As noted above, in one embodiment the cleaning step is preferably carried out with cyclical phase modulation (CPM), or while cyclically modulating/changing the phase of the cleaning composition (i.e., cyclically changing the phase of the cleaning composition from liquid to gas, liquid to supercritical, supercritical to gas, supercritical to liquid, etc.). CPM employs processing controls of the CO_2 dense phase/cleaning composition that result in (1) enhanced physical and (2) enhanced chemical action on resists, resist residues, organic residues, particulate matter, and the like. With respect to 1), liquid and supercritical CO_2 plasticize organic polymers whereby CO_2 permeates the bulk phase at a molecular level, augmenting intra- and inter- molecular bonding interactions. During CPM, as the density of the fluid is modulated up and down, carbon dioxide mass diffuses in and back out of the polymer bulk phase. This process causes mechanical stresses and strains on the bulk polymer that facilitate expansion, contraction, delamination, potentially dissolution, and ultimately removal of polymeric materials from surfaces. Since dense carbon dioxide cleaning is preferably enhanced using co-solvents, surfactants, reactants, and sometimes water, the dense phase must also be a good carrier for these materials. With respect to 2), CPM is used to control the partitioning of chemical adjuncts in A) the continuous phase, B) at the surface of the substrate, and C) in the bulk-phase of the material to be removed, such as the resist residue.

Many organic materials are soluble in liquid and/or supercritical CO_2 under ranges of conditions of temperature (T) and pressure (P), otherwise noted as continuous-phase density. Solubility of materials in these ranges is also concentration dependent. Water along with highly polar low vapor pressure materials, and inorganic materials are typically insoluble in liquid and supercritical CO_2. However, surfactants with CO_2-philic character have been shown to be very useful in dispersing and emulsifying these materials in dense CO_2. Furthermore, conventional surfactants that do not contain fluorinated or siloxane-based components have been shown to to be useful in dense phase CO2 when combined with certain co-solvent modifiers. During CPM, as the density of the continuous phase modulates, chemical adjuncts dissolved, dispersed, or emulsified therein partition between the continuous phase and the surface of the substrate. Furthermore, CO_2 plus adjuncts in the bulk phase of polymeric and porous residues can, as a result of CPM, diffuse out of bulk materials at different rates, concentrating the adjuncts in the bulk phase. This concentrating effect in the bulk phase kinetically enhances swelling and dissolution of residues. For example, consider the case of an organic polymer residue that contains polar hydrogen bonding functional groups that inhibit swelling and dissolution in dense CO_2. A soluble hydrogen bonding co-solvent can be employed with CO_2 to enhance the swelling of the bulk polymer and ultimately the removal of the materials from a substrate. However, the swelling and dissolution or dispersion of this material is limited kinetically by the concentration of the adjunct in CO2. With CPM, conditions of (T) and (P) can be manipulated to cause partitioning between the continuous phase and the surface of the wafer, and in the bulk phase of the residue. This process increases the localized concentration of adjuncts in and on residues at a molecular level. This concentrating effect, represents and kinetic advantage over solutions, dispersions, or emulsion of adjuncts in dense CO2.

In summary, CPM with dense phase carbon dioxide and chemical adjuncts, enhances the removal of resists, resists residues, particulate, and organic materials by enhancing physical and chemical action on these materials encountered during the manufacturing of microelectronic substrates.

Cyclical Phase Modulation (CPM) during an example wafer cleaning process. During the manufacturing of an integrated circuit, a semiconductor wafer is

cleaned after an etch step in the following process, **Figure 4**, using dense phase carbon dioxide. Dense carbon dioxide is stored in pressure vessel (I) (**50**) at conditions of between 300 and 5000 psi and a temperature of between –20°C and 100°C, further described as the high-pressure vessel. A wafer is loaded into cleaning chamber (III) (51) in an automated or manual fashion where the wafer is held on a platform (XI) (52) connected to a chuck and a sealed shaft (not shown) so that the platform can spin. Located above the wafer held on the platform is a spray bar (X) (53) designed to disperse the flow of dense phase carbon dioxide and chemical adjuncts and to direct substantial fluid action onto the surfaces of the wafer. Cleaning chamber (III) is pressurized with clean carbon dioxide from either a bulk storage tank (XII) (**54**) through valve (i) (**55**) or from pressure vessel (I) (**50**) through valve (a) (**56**) to a pressure of between 300 psi and 5000 psi at a temperature of between –20°C and 100°C. The temperature of the dense CO_2 can be modulated using heat exchanger (II) (**60**). Additionally, the temperature of the processing phase in chamber (III) (**51**) can be modulated using heat exchangers internal or external to the chamber. Highly filtered chemical adjuncts as required are added to cleaning chamber (III) (**51**) from adjunct addition module (VI) (**61**) through valve (b) (**62**) during the addition of dense CO_2 or alternatively prior to the addition of the dense CO_2. The adjunct addition module serves to store, filter, mix and sequentially or simultaneously meter adjunct materials to the cleaning chamber. During the cleaning process, the dense phase CO_2 is optionally circulated from the cleaning chamber through valve (e) (**66**) using pump (VII) (**63**) through solid separation filter (VIII) (**64**) and valve (f) (**65**) back into the chamber through the spray bar (X) (**53**). During the circulation the wafer can be spun at rates between zero and 3000 rpm. Also during the cleaning step, the density of the system is cyclically modulated. This can be accomplished with the following sequence. Pressure vessel (I) (**50**), the high-pressure vessel, containing dense CO_2, is maintained at a pressure notably above (50 to 2000 psi greater than) that of cleaning chamber (III) (**51**). Pressure vessel (V) (**70**), low-pressure vessel, is held at a pressure notably less than (50 to 3000 psi lower than) cleaning chamber (III) (**51**), and the temperature of the independent vessels are roughly the same. In the cyclical process, valve (a) (**56**) is first opened to allow for the flow of mass between (I) and (III) then closed. Valve (d) (**71**) is then opened to allow for the flow of mass between (III) and

(V). Valve (g) **(72)** is then opened to separator/abatement module (IX) (73) such as a filter or other separator that serves to separate chemical adjuncts from CO_2 and removed waste. The abatement module also allows for removed CO_2 mass to be re-added to tank (I) through valve (h) **(74)** completing the mass flow cycle. Alternatively, CO_2 mass can be added to pressure vessel (I) from bulk storage, to reestablish higher pressure in vessel (I) than chamber (III). This mass flow cycle is repeated multiple times (between 1 and 500) in a given cleaning cycle resulting in cyclical phase modulation (CPM). Dense CO_2 circulation in cleaning chamber (III) can optionally be augmented using pump (VII) and valves (e) and (f) during CPM. During the cleaning step, CPM can be alternatively achieved using variable volume chamber (IV) **(80)** with valve (c) **(81)** opened. In this scenario, the volume of (IV) is increased and reduced cyclically, between 1 and 500 times in a given cleaning cycle. In this CPM scenario, fluid can optionally be circulated through the cleaning chamber (III) using pump (VII) and valves (e) and (f). After a period sufficient to remove the contaminants from the surface of the wafer, dense phase CO_2 mixture is flushed from the system through valve (d) into vessel (V) with addition of pure dense phase CO_2 from tank (I) through valve (a). This rinse process continues until all adjunct and waste are removed from the chamber. The dense CO_2 is vented from cleaning chamber (III) to a waste or abatement system.

Water soluble compounds to deliver. Examples of water soluble compounds to be delivered to facilitate cleaning in embodiments employing water in the cleaning system as described above include, but are not limited to: Acids (including but not limited to HF, HF/NH_4F (also known as "BOE"- buffered oxide etch or "BHF"- buffered HF), H_2SO_4, HCl, HBr, H_3PO_4, HNO_3, CH_3CO_2H, $H_2S_2O_8$, KCN, KI, etc.); Reactants (including but not limited to H_2O_2, NH_4F and NH_4F_2, $SiCl_4$, $SiHCl_3$, $Si(C_2H_5O)_4$, Br, I, EDTA, Surfactants, $(NH_4)_2SO_4$, O_3, H_2, SO_3, N_2O, NO, NO_2, F_2, Cl_2, Br_2 etc.); Alkalis or bases (including but not limited to NH_4OH, KOH, NaOH, etc.); Weak Bases and ion pairs (including but not limited to Choline $(CH_3)_3N^+(CH_2CH_2OH \cdot OH)$, Tertiary Amines, etc.) and combinations thereof.

Methods for the Control of Contaminants Following Carbon Dioxide Cleaning of Microelectronic Structures. Contaminants removed from surfaces features of microelectronic substrates after ion implantation, 'back end of the line'

(BEOL) cleaning processes , 'front end of the line' (FEOL) cleaning processes, and post CMP steps vary in nature and composition dramatically. Accordingly, cleaning steps must address these contaminants with the appropriate chemistries and solvents to either react with, ionize, dissolve, swell, disperse, emulsify, or vaporize them from the substrate. As such, a variety of water and solvent-based systems, and dry cleaning processes exist to address the broad variety of waste materials.

Common to all cleaning processes, however, is the need to completely remove all contaminants, and adjuncts from the substrate leaving the substrate free, substantially free or essentially free of organic, inorganic, metallic, or composite waste mater (*e.g.*, the amount of contaminants left after the process is completed is not more than 5%, 1%, 0.5%, 0.1%, 0.05%, 0.01%, 0.005%, 0.001%, or less, by weight of the amount of contaminant prior to the cleaning process)). These foreign materials often seen in residues from wet-cleaning processes, often referred to as watermarks, can dramatically and detrimentally affect the ultimate performance of integrated circuits and other microelectronic devices. This is traditionally minimized in wet-cleaning and solvent based cleaning processes by using copious amounts of ultra-pure water and/or solvents for rinse steps. In these processes, fluid streams are directed in a fashion that sweeps contaminants away from the substrate such that re-deposition of mater is minimized. These rinsing practices result in large quantities of aqueous and solvent-based waste streams that are increasing as device feature sizes continue to shrink. Vapor-phase dryers, such as IPA dryers, are also commonly used to minimize the occurrence of watermarks or water-spots.

Liquid and supercritical CO_2-based cleaning and drying processes have been proposed in the manufacturing of microelectronic substrates. Processing methodologies that effectively eliminate the redeposition of contaminants onto and into the surface features of microelectronic substrates during or subsequent to cleaning steps are needed. The processes disclosed herein accomplish this task while also advantageously minimizing the extraneous use of processing rinse fluid that would result from patterned flow and waste scenarios. **Figure 5** represents a basic process diagram for a general description of this embodiment of the invention.

During or carbon dioxide cleaning steps fluid in the chamber may be in the supercritical state or the liquid state. Furthermore, liquid CO_2 compositions can be at

the saturation point, termed saturated liquid CO_2 (liquid and gas co-existing in some proportion), or it can be compressed (no liquid meniscus). For the purposes of this invention each scenario will be described separately.

Removing supercritical CO_2 compositions and contaminants from cleaning chambers avoiding re-deposition of cleaning adjuncts and contaminants and minimizing rinse volumes.

Cleaning steps using CO_2 may use a variety of chemical adjuncts including co-solvents, surfactants, reactants, water, and combinations of some or all to enable or facilitate the quantitative removal of contaminants. These materials may be suspended, dissolved, dispersed, or emulsified in the carbon dioxide continuous phase. The stability of suspensions, dispersions, emulsions, and even solutions of materials in supercritical CO_2 as well as liquid is largely a function of CO_2 fluid density. Generally speaking, as the density of the CO_2 continuous phase decreases the stability of suspensions, dispersions, or emulsions also decrease. Since removal of CO_2 mass through draining or venting of the cleaning chamber mandates gradual to rapid reductions in fluid density, this process can result in the undesirable collapse of materials, termed redeposition in the case of contaminants and deposition in the case of adjuncts, onto the substrate. Consistent with conventional cleaning processes, copious amounts of ultra-pure rinse fluid, in this case CO_2, can be used to dilute the adjunct plus contaminant mixture prior to the venting step such that minimal redeposition is encountered. This can be disadvantageous based on required fluid volumes and processing cycle times.

The current invention circumvents the above-described problems as described in the context of **Figure 5.** Supercritical processing fluid containing some level of contaminants and/or adjuncts either prior to a rinse step or subsequent to a rinse step is removed without deposition or redeposition of materials onto the substrate. Chamber I (**50**) represents the cleaning chamber. Pressure vessel II (**51**) represents a storage tank for processing fluid after cleaning. It can be integrated with abatement or recycling systems as desired. Subsystem III (**52**) represents a source of clean (*i.e.*, sufficiently clean to achieve the desired level of cleanness/lack of redeposition of contaminants on the substrate) gaseous or supercritical components that can be a secondary gas with a saturated vapor pressure that exceeds that of carbon dioxide, or

can be heated carbon dioxide in the supercritical phase or gas phase. Exemplary secondary gases include: helium, nitrogen, argon, and oxygen, or mixtures thereof. In the present invention, contaminated supercritical fluid is removed from the processing chamber by providing a secondary source of gas from system III 52 through valve (b) 53 at a pressure that exceeds the pressure in the processing chamber (I). Rapid mixing of the secondary gas with the supercritical fluid will transition the continuous phase to a liquid composition. Nearly simultaneous with the opening of valve (b), valve (c) 54 is opened between chamber (I) and vessel (II) to allow for removal of the CO_2 plus contaminants in a plug flow or draining fashion. Valve (b) remains open providing chamber (I) a continuous flow of secondary gas until all fluid mater is forced from chamber (I) at which point valves (b) and (c) are closed. Throughout this operation, the pressure in vessel (II) is maintained at a lower pressure than chamber (I).

Alternatively, system (III) can supply the chamber (I) with a heated source of supercritical CO_2 at a pressure and temperature that exceeds that of the processing fluid in chamber (I). Ideally the supercritical CO_2 added from system (III) has a lower density than that in chamber (I). In this case, the mixing of CO_2 fluids of varied density is accompanied by rapid flow of mass out of chamber (I) into vessel (II). The flushing action removes CO_2 plus contaminants from the cleaning chamber. The process can be used as a final drain followed by a vent or in conjunction with a series of fill and drain sequences preceding a final vent.

Removing liquid CO_2 compositions and contaminants from cleaning chambers avoiding re-deposition of cleaning adjuncts and contaminants and minimizing rinse volumes.

Liquid CO_2 compositions can be removed from cleaning chambers without the deposition of adjuncts or redeposition of contaminants using the following sequence that incorporate a secondary gas such as helium or nitrogen, or gaseous or supercritical CO_2. In the first case, liquid compositions are removed from chamber (I) by first opening valve (b) to system (III) where system (III) contains a secondary gas at a pressure greater than that in chamber (I). Nearly simultaneously or shortly after, valve (c) 54 is opened between chamber (I) and vessel (II) allow for forced plug flow of the liquid composition from chamber (I). After complete removal of liquid from (I), valves (c) 54 and (b) 53 are closed. This process can be used as a final removal

drain step prior to venting or in a sequence of fill and drain steps. Alternatively, heated gaseous CO_2 or supercritical CO_2 is supplied from system (III) using the same process steps. In the case of gaseous CO_2 the pressure and temperature of the gas must exceed that of the processing fluid in chamber (I) to be removed. In the case of supercritical CO_2 being supplied by system (III), the fluid is supplied at a temperature and pressure that exceeds that of the fluid in chamber (I) so long as the density of the fluid is less than that of the liquid in chamber (I). Any condensation of gas or supercritical CO_2 to a liquid as mass rapidly flows from (III) to (I) to (II) may benefit the process by providing a surface rinsing action during the drain flush step. Again, this process can be used as a final removal or flush step prior to chamber venting or in a series of fill and drain steps preceding a final vent.

Alternatively, if the cleaning chamber is using liquid CO_2 compositions at saturated vapor pressure the fluid composition can be drained in the following steps to avoid deposition of materials onto the substrate surface. In this case, liquid CO_2 at saturated vapor pressure is maintained in vessel (II) prior to the draining or flushing step. The liquid composition is drained from (I) by first opening valve (e) 55 connecting the vapor-phase side of (I) with the vapor-phase side of (II), then opening valve (c) 54 connecting the liquid side of (I) with the vapor side of (II). By force of gravity, this allows the flow of liquid out of (I) without boiling liquid in chamber (I). The boiling of liquid is prevented to avoid the deposition of entrained materials onto surfaces. Vapor side communication (i.e., a vapor communication passage to permit vapor flow) is preferably provided between the two chambers. Once again, this process can be used as a final removal or drain step prior to chamber venting or in a series of fill and drain steps preceding a final vent.

The present invention is explained in greater detail in the following non-limiting Examples

COMPARATIVE EXAMPLE A

Treatment of a Coated Wafer with Liquid Carbon Dioxide

A CO_2-miscible, hydrophilic solvent, such as isopropanol (IPA), was added to a high-pressure vessel that contained a piece of a poly(hydroxystyrene) (PHS) coated silicon wafer. Liquid CO_2 was added to the high-pressure vessel. As the liquid

CO_2/IPA (2 % IPA by volume) mixture meniscus level rose above the surface of the wafer, damage to the wafer was observed. After the system was mixed for 15 minutes, the liquid CO_2/IPA mixture was drained from the bottom of the high-pressure vessel. More damage to the wafer was observed as the IPA boiled at the liquid/gas/wafer interface.

EXAMPLE 1

Treatment of a Coated Wafer with Liquid Carbon Dioxide

Liquid CO_2 was added to a high-pressure vessel that contained a piece of a PHS coated silicon wafer until the wafer was completely submerged in liquid CO_2. A mixture that contained liquid CO_2 and IPA, 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent, or any hydrophilic/CO_2-philic surfactant) was added to the high-pressure vessel that contained the piece of PHS coated silicon wafer submerged in liquid CO_2. No damage to the wafer was observed. The system was mixed for 15 minutes. There was still no damage to the wafer. A secondary gas (helium or nitrogen) was added to the top of the high-pressure vessel. The liquid CO_2/IPA mixture was drained under the pressure of the secondary gas to prevent boiling at the liquid/gas/wafer interface. There was no damage to the wafer after the system was drained with a secondary gas. The system was rinsed with pure liquid CO_2 and was then drained as mentioned above. There was no damage to the wafer.

EXAMPLE 2

Treatment of a Coated Wafer with Liquid Carbon Dioxide

Liquid CO_2 at its saturated vapor pressure was added to a high-pressure vessel that contained a piece of a PHS coated silicon wafer until the wafer was completely submerged in liquid CO_2. A mixture that contained liquid CO_2 and IPA, 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent, or hydrophilic/CO_2-philic surfactant) was added to the high-pressure vessel that contained the piece of PHS coated silicon wafer submerged in liquid CO_2. No damage to the wafer was observed. The liquid CO_2 mixture was drained from the high-pressure vessel to another high-pressure vessel containing predominantly liquid CO_2 at saturated vapor pressure by first opening a valve connecting the vapor side of both vessels then by

opening a valve connecting the liquid side of both vessels. The liquid was drained by force of gravity as the first vessel was positioned substantially above the second to allow for complete drainage. No damage was observed. Pure liquid CO_2 was added to the vessel containing the wafer segment as a rinse, and that liquid was subsequently drained in the manor described above. Again, no damage was observed.

EXAMPLE 3

Treatment of a Coated Wafer with Liquid and Supercritical CO_2

Liquid CO_2 was added to a high-pressure vessel that contained a piece of a PHS coated silicon wafer until the wafer was completely submerged in liquid CO_2. A mixture that contained liquid CO_2 and IPA, 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent or surfactant that increased the carry capacity of CO_2 for water) was added to the high-pressure vessel that contained the piece of PHS coated silicon wafer submerged in liquid CO_2. No damage to the wafer was observed. After a period of time sufficient to remove the substantial majority of the water from the surface of the wafer, the liquid mixture was diluted with pure liquid CO_2 to effect approximately 5 liquid turnovers in the drying chamber. Heat was then added to the liquid CO_2 causing a transition to the supercritical phase. The chamber containing the wafer is then drained and vented by maintaining the temperature of fluid and gas above the critical temperature of CO_2, thus avoiding the liquid phase. The wafer was removed from the chamber with no damage.

EXAMPLE 4

Treatment of a Coated Wafer with Supercritical Carbon Dioxide

Supercritical CO_2 was added to a high-pressure vessel that contained a piece of a PHS coated silicon wafer. A mixture that contained supercritical CO_2 and IPA, 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent or surfactant that increased the carry capacity of CO_2 for water) was added to the high-pressure vessel that contained the piece of PHS coated silicon wafer and supercritical CO_2. No damage to the wafer was observed. The system was mixed for 15 minutes. There was still no damage to the wafer. A secondary gas (helium or nitrogen) was added to the top of the high-pressure vessel until the system became subcritical and a liquid

meniscus was formed. The liquid CO_2/IPA mixture was drained under the pressure of the secondary gas to prevent boiling at the liquid/gas/wafer interface. There was no damage to the wafer after the system was drained with a secondary gas. The system was rinsed with pure liquid CO_2 and was then drained as mentioned above. There was no damage to the wafer.

COMPARATIVE EXAMPLE B

Solvation of Water from a Coated Wafer with Liquid Carbon Dioxide

A droplet of water was dripped on top of a piece of a PHS coated silicon wafer. The wafer that contained the water droplet was placed in the high-pressure view cell. Pure liquid CO_2 was added to the high-pressure vessel. The system was mixed for 15 minutes. The liquid CO_2 did not solvate the entire droplet of water as determined visually through a sapphire window on the view cell.

EXAMPLE 5

Solvation of Water from a Coated Wafer with Liquid Carbon Dioxide and Cosolvent

A droplet of water was dripped on top of a piece of a PHS coated silicon wafer. The wafer that contained the water droplet was placed in the high-pressure view cell. Liquid CO_2 was added to a high-pressure vessel that contained a piece of a PHS coated silicon wafer until the wafer was completely submerged in liquid CO_2. A mixture that contained liquid CO_2 and IPA, 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent) was added to the high-pressure vessel that contained the piece of PHS coated silicon wafer submerged in liquid CO_2. No damage to the wafer was observed. The system was mixed for 15 minutes. The water droplet was completely solvated. There was still no damage to the wafer. A secondary gas (helium or nitrogen) was added to the top of the high-pressure vessel. The liquid CO_2/IPA mixture was drained under the pressure of the secondary gas to prevent boiling at the liquid/gas/wafer interface. There was no damage to the wafer after the system was drained with a secondary gas. The system was rinsed with pure liquid CO_2 and was then drained as mentioned above. There was no damage to the wafer.

EXAMPLE 6

Solvation of Water from a Coated Wafer with Liquid and Supercritical Carbon Dioxide and Cosolvent

A whole 5" PHS coated wafer wetted with water, as it would be in an aqueous post-development process, was placed in the prototype drying chamber. The chamber was filled with liquid carbon dioxide. The prototype system contained a second high pressure vessel , containing liquid CO_2 plus 2 % IPA by volume, (alternatively any CO_2-miscible, hydrophilic solvent or surfactant that increased the carry capacity of CO_2 for water) The mixed liquid CO_2/IPA was added to the drying chamber from the second high-pressure vessel using a pump. The system was mixed for 15 minutes. The liquid CO_2/IPA mixture was flushed with 5 liquid turnovers of pure liquid CO_2 so that the concentration of IPA dropped to a fraction of its previous concentration. There was no meniscus formation during the CO_2 flush. After the CO_2 flush, the liquid CO_2 was heated to 35°C transitioning the fluid to a supercritical phase. The supercritical CO_2 was then drained/vented from the vessel as heat was added to maintain the fluid, and subsequently the gas, above the critical temperature of CO_2. When the chamber was completely vented the wafer was removed dry and undamaged.

EXAMPLE 7

Drying of Water from an Imaged and Aqueously Developed Resist-Coated Wafer Using CO_2 and Chemical Adjuncts

A 5-inch silicon wafer coated with a PHS photoresist and a PAG was imaged, developed using 0.238 normal tetramethyl ammonium hydroxide, and rinsed with deionized water. The wet wafer was then transferred to a high-pressure drying chamber, where liquid CO_2 at saturated vapor pressure was added in a small amount. Additional liquid CO_2 at saturated vapor pressure premixed with a hydrophilic/CO_2-philic surfactant was added to and circulated through the chamber to displace and remove the water from the surface of the wafer and features of the resist pattern. After a short period of time the liquid was drained to a secondary storage vessel containing a small amount of liquid CO_2 first by allowing a vapor-side

communication between the two vessels then by opening a valve connecting the bottom of the drying vessel with the bottom of the second storage vessel. The second storage vessel was position sufficiently below the drying chamber that the majority of the liquid drained from the drying chamber. The drying chamber was then filled with pure liquid CO_2 as a rinse followed by draining as described above. This was repeated to insure that the concentration of the adjunct was effectively zero. The small amount of remaining liquid CO_2 in the drying chamber was heated to above its critical point, 35oC, and the CO_2 was vented while maintaining the fluid/gas temperature above the critical temperature thus avoiding the formation of a liquid meniscus. The imaged, developed, and dried wafer was then removed from the chamber, stored in the absence of light and moisture, and then analyzed using a scanning electron microscope. The micrograph showed that the developed features, demonstrating line/ space patterns of less than 120 –nm, were consistent structurally unaffected by the CO_2 drying process.

EXAMPLE 8

MEM's Water and Contaminant Removal

During the manufacturing of a MEM's device containing a series of electrostatic actuators, a sacrificial oxide layer is removed using aqueous hydrofluoric acid, exposing a series of pivoting plates parallel to the substrate surface. After a sequential rinse step, the device is transferred to a high-pressure CO_2-based drying chamber, where a liquid CO_2 mixture is added at saturated vapor pressure. The liquid CO_2 contains a CO_2-philic/hydrophilic surfactant that is premixed with the CO_2 to ensure a homogeneous composition. After a period of circulation, pure liquid CO_2 is fed into the chamber as liquid CO_2, surfactant, water and entrained solutes are removed from the vessel at constant pressure. The liquid CO_2 remaining in the chamber is then heated to above its critical temperature converting the fluid into the supercritical state. The supercritical fluid in the processing chamber is then vented into a storage tank serving to ensure that the temperature of the fluid/gas mixture stays above the critical temperature of CO_2. This serves to ensure that the liquid state, a liquid meniscus, and associated surface tension are avoided during the draining/venting step. An SEM analysis of the MEM's device shows that the pivoting

plates are all substantially parallel to the substrate surface with no evidence of release stiction.

EXAMPLE 9

Post CMP Cleaning

Polishing slurry, polishing residues and particulates are removed post-CMP using the following process steps. The substrate, a semiconductor wafer with a metal or dielectric surface, is loaded into a pressure vessel. An aqueous solution of hydrogen peroxide (30% concentration in water) in a liquid CO_2 emulsion containing a high purity CO_2-philic-b-hydrophilic surfactant is introduced at 1,200 psi and room temperature. Cyclical phase modulation is used to condense the emulsion onto the surface of the wafer followed by re-emulsification. This is accomplished by increasing the effective volume of the cleaning chamber causing a reduction in pressure from 1200 psi at room temperature to 790 psi at about 15 C. The volume is increased using an automated variable volume cylinder and appropriate valves. The aqueous cleaning solution is condensed onto the surface of the wafer for a short period of time as the density of the liquid CO_2 is reduced. The pressure is then increased by a reduction of vessel volume restoring the pressure in the cleaning chamber to 1200 psi. The cycle is repeated 20 times. The first solution is then displaced from the vessel by a second cleaning solution consisting of an aqueous fluoride in CO_2 emulsion with a high purity CO_2-philic-b-hydrophilic surfactant. The pressure is then modulated cyclically as above, 20 times. Supercritical CO_2 at 1800 psi and 40 C, with a high purity surfactant is then flowed through the vessel to facilitate the removal of any remaining particulates. A supercritical CO_2 rinse is then completed by addition of pure CO_2 to the vessel. The system is vented a final time and the substrate is removed.

EXAMPLE 10

Polishing slurry, polishing residues and particulates are removed post-CMP using the following process steps. The substrate, a semiconductor wafer with a metal or dielectric surface, is loaded into a pressure vessel. An aqueous solution of hydrogen peroxide in a liquid CO_2 emulsion containing a high purity CO_2-philic-b-

hydrophilic surfactant is introduced at 1,200 psi and room temperature. The aqueous cleaning solution is condensed onto the surface of the wafer for a short period of time using a variable volume chamber connecting to the cleaning vessel. The pressure is then increased by a reduction of vessel volume to restore the pressure to the original value. The cycle is repeated 20 times. The first solution is displaced from the vessel by a second cleaning solution consisting of an aqueous fluoride in CO_2 emulsion with a high purity CO_2-philic-b-hydrophilic surfactant. The pressure is then modulated as above 20 times using a variable volume chamber. Supercritical CO_2 containing a small amount CO_2-soluble chelating agent (ethylenediaminetetraacetic acid) is then flowed through the vessel to facilitate the removal of any remaining metal ions. Supercritical CO_2 with a high purity surfactant is then flowed through the vessel to facilitate the removal of any remaining particulate mater. A supercritical CO_2 rinse is then completed by addition of pure CO_2 to the vessel. The system is vented a final time and the substrate removed.

EXAMPLE 11

Photoresist is used to pattern substrates for ion implantation. The photoresist used for this process is removed in the following steps. The substrate, a semiconductor post ion implantation, is loaded into a pressure vessel. Supercritical CO_2 is added to the vessel at 3,000 psi and 35 °C. As the supercritical CO_2 circulated through the vessel, a co-solvent mixture consisting of triethanolamine, N-methyl-2-pyrrolidone, a surfactant containing both CO_2-philic and hydrophilic components, and water are added. The mixture composition by weight is 7:2:1:1, and the total concentration of adjunct added is 2.5% w/v of the fluid system. The pressure of the vessel is reduced using a variable volume chamber and appropriate valves causing an expansion of the processing fluid in the cleaning chamber and thereby condensing a concentrated mixture of the adjunct mixture onto the surface of the substrate. The temperature of the mixture drops below the T_c in the course of the expansion causing a transition to liquid CO2. The system is re-pressurized and the fluid mixture heated above T_c again using the variable volume chamber and internal heaters. This cycle is repeated 20 times and followed by a pure supercritical CO_2 rinse. The system is vented and the substrate removed.

EXAMPLE 12

Polymeric photoresist and resist residue is removed from via structures of a test wafer after reactive ion etching using the following process steps. An amine (triethylamine) in supercritical CO_2 plus a high purity surfactant with both a CO_2-philic and an oleophilic segment is added to the vessel at 3,000 psi at 60 °C (2% w/v amine, 1% w/v surfactant). The fluid mixture is circulated through the vessel. The pressure of the fluid mixture is rapidly reduced to 1,500 psi thereby condensing the adjunct onto the surface of the substrate. The pressure is then rapidly increased back to 3,000 psi re-dispersing all chemical adjuncts. The cycle is repeated 20 times using a variable volume chamber. Heat is added to the chamber using an internal heater to maintain the temperature as near to 60 °C as possible. Helium gas at 3500 psi was then added to the cleaning chamber as a valve at the bottom of the chamber was opened to a waste vessel. The processing fluid was rapidly flushed from the chamber and replaced by a pressurized atmosphere of pure helium. After the helium was vented off the cleaning vessel was rinsed with pure supercritical CO_2 A second cleaning solution consisting of a co-solvent (2,4-pentanedione, 3% w/v total) and a high purity surfactant (1% w/v) was added to the cleaning vessel with CO_2 at 3000 psi and 60 C. The pressure of the system is modulated as described above 20 times while the temperature of the fluid is maintained as close to 60 °C as possible using an internal heater. The cleaning fluid was drained as above using helium as a secondary gas. Finally, a pure supercritical CO_2 rinse is completed, the system was drained using helium as a secondary gas and then vented, and the substrate removed.

The foregoing is illustrative of the present invention, and is not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

THAT WHICH IS CLAIMED IS:

1. A method of cleaning a microelectronic device, comprising the steps of:

providing a substrate having a surface portion to be cleaned,

providing a densified carbon dioxide cleaning composition, said drying composition comprising carbon dioxide and a cleaning adjunct, said cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

immersing said surface portion in said densified carbon dioxide composition; and then

removing said cleaning composition from said surface portion; while

maintaining said cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step.

2. The method according to claim 1, wherein said microelectronic device comprises a microelectromechanical device.

3. The method according to claim 1, wherein said microelectronic device comprises an optoelectronic device.

4. The method according to claim 1, wherein said microelectronic device comprises a resist-coated substrate.

5. The method according to claim 1, wherein said carbon dioxide is supercritical carbon dioxide.

6. The method according to claim 1, wherein said cleaning adjunct comprises a co-solvent.

7. The method according to claim 6, wherein said co-solvent comprises an alkane, an alcohol, or a combination thereof.

8. The method according to claim 1, wherein said cleaning adjunct comprises a surfactant.

9. The method according to claim 8, wherein said surfactant contains a CO_2-philic group.

10. The method according to claim 8, wherein said surfactant does not contain a CO_2-philic group.

11. The method according to claim 1, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

12. The method according to claim 11, wherein said immersing step is carried out while maintaining said cleaning composition as a homogeneous solution.

13. The method according to claim 12, wherein said removing step is carried out while maintaining said cleaning composition as a homogeneous solution.

14. The method according to claim 1, wherein said cleaning composition is a liquid cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

15. The method according to claim 14, wherein said second compressed gas is selected from the group consisting of helium, nitrogen, and air.

16. A method according to claim 14, wherein a second compressed gas with a lower heat of compression than CO_2 is used during said draining step to displace liquid and gaseous CO_2, thereby leaving a majority of said second gas in the vapor phase and serving to prevent thermal shock upon subsequent venting thereof.

17. The method according to claim 1, wherein said cleaning composition is a supercritical cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical cleaning composition so that it is converted to a liquid cleaning composition.

18. The method according to claim 1, wherein said removing step is carried out by diluting said cleaning composition with additional carbon dioxide.

19. A method according to claim 1, wherein a said cleaning step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2 and then heated to produce a supercritical fluid, after which said supercritical fluid is removed while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

20. A method according to claim 1, wherein said cleaning comprises removal of water from said device.

21. A method of removing water from a resist-coated substrate, comprising the steps of:

providing a substrate having a resist coating formed on a surface portion thereof, and having water on said resist coating;

providing a densified carbon dioxide drying composition, said drying composition comprising carbon dioxide and a drying adjunct, said drying adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

immersing said surface portion in said densified carbon dioxide drying composition; and then

removing said drying composition from said surface portion;

and wherein said drying composition is maintained as a homogeneous composition during said immersing step and said removing step.

22. The method according to claim 21, wherein said substrate comprises a semiconductor substrate.

23. The method according to claim 21, wherein said resist comprises a polymeric material.

24. The method according to claim 21, wherein said resist is selected from the group consisting of positive-acting resists and negative-acting resists.

25. The method according to claim 21, wherein said resist is a patterned resist.

26. The method according to claim 21, wherein said carbon dioxide is liquid carbon dioxide.

27. The method according to claim 21, wherein said carbon dioxide is supercritical carbon dioxide.

28. The method according to claim 21, wherein said drying adjunct comprises a co-solvent.

29. The method according to claim 28, wherein said co-solvent comprises an alkane, an alcohol, or a combination thereof.

30. The method according to claim 21, wherein said drying adjunct comprises a surfactant.

31. The method according to claim 30, wherein said surfactant contains a CO_2-philic group.

32. The method according to claim 30, wherein said surfactant does not contain a CO_2-philic group.

33. The method according to claim 21, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

34. The method according to claim 33, wherein said immersing step is carried out while maintaining said drying composition as a homogeneous solution.

35. The method according to claim 33, wherein said removing step is carried out while maintaining said drying composition as a homogeneous solution.

36. The method according to claim 31, wherein said drying composition is a liquid drying composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

37. The method according to claim 36, wherein said second compressed gas is selected from the group consisting of helium, nitrogen, and air.

38. A method according to claim 36, wherein a second compressed gas having a lower heat of compression than CO_2 is used during said draining step to displace liquid and gaseous CO_2, leaving a majority of the secondary gas in the vapor phase and serving to prevent thermal shock upon subsequent venting thereof.

39. The method according to claim 21, wherein said drying composition is a supercritical drying composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical drying composition so that it is converted to a liquid drying composition.

40. The method according to claim 21, wherein said removing step is carried out by diluting said drying composition with additional carbon dioxide.

41. A method according to claim 21, wherein a said drying step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2, then heated to produce a supercritical fluid, after which said fluid is removed from the drying chamber while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

42. A method according to claim 21, where said drying step is preceded by a development step that incorporates aqueous developers and pure water in the same chamber used to in the drying step.

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43. A method of cleaning contaminants from a microelectronic device, comprising the steps of:

providing a substrate having a surface portion to be cleaned,

providing a densified carbon dioxide cleaning composition, said cleaning composition comprising carbon dioxide and a cleaning adjunct, said cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

immersing said surface portion in said densified carbon dioxide cleaning composition; and then

removing said cleaning composition from said surface portion;

and while cyclically modulating the phase of said cleaning composition during at least a portion of said immersing step.

44. The method according to claim 43, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said secondary gas.

45. The method according to claim 43, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing clean heated supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said heated supercritical CO_2.

46. The method according to claim 43, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said liquid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said secondary gas.

47. The method according to claim 43, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing clean heated gas or supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said heated gas or supercritical CO_2.

48. The method according to claim 43, wherein said densified cleaning composition is a liquid and is at saturated vapor pressure, and said removing step is carried out by draining said liquid.with vapor side communication between said cleaning chamber and a receiving vessel.

49. The method according to claim 43, further comprising:

maintaining said cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step.

50. The method according to claim 43, wherein said microelectronic device comprises a microelectromechanical device.

51. The method according to claim 43, wherein said microelectronic device comprises an optoelectronic device.

52. The method according to claim 43, wherein said microelectronic device comprises a resist-coated substrate.

53. The method according to claim 43, wherein said carbon dioxide is supercritical carbon dioxide.

54. The method according to claim 43, wherein said cleaning adjunct comprises a co-solvent.

55. The method according to claim 43, wherein said cleaning adjunct comprises a surfactant.

56. The method according to claim 43, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

57. The method according to claim 43, wherein said cleaning composition is a liquid cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

58. The method according to claim 43, wherein said cleaning composition is a supercritical cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical cleaning composition so that it is converted to a liquid cleaning composition.

59. The method according to claim 43, wherein said removing step is carried out by diluting said cleaning composition with additional carbon dioxide.

60. A method according to claim 43, wherein a said cleaning step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2 and then heated to produce a supercritical fluid, after which said supercritical fluid is removed while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

61. A method according to claim 43, wherein said cleaning comprises removal of water from said device.

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62. A method of cleaning contaminants from a microelectronic device,. comprising the steps of:

providing a substrate having a surface portion to be cleaned,

providing a densified carbon dioxide cleaning composition, said cleaning composition comprising carbon dioxide, water and a water-soluble cleaning adjunct,

immersing said surface portion in said densified carbon dioxide cleaning composition; and then

removing said cleaning composition from said surface portion

63. The method according to claim 62, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said secondary gas.

64. The method according to claim 62, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing clean heated supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said heated supercritical CO_2.

65. The method according to claim 62, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said liquid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said secondary gas.

66. The method according to claim 62, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing clean heated gas or supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said heated gas or supercritical CO_2.

67. The method according to claim 62, wherein said densified cleaning composition is a liquid and is at saturated vapor pressure, and said removing step is carried out by draining said liquid with vapor side communication between said cleaning chamber and a receiving vessel.

68. The method according to claim 62, further comprising:

maintaining said cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step.

69. The method according to claim 62, wherein said microelectronic device comprises a microelectromechanical device.

70. The method according to claim 62, wherein said microelectronic device comprises an optoelectronic device.

71. The method according to claim 62, wherein said microelectronic device comprises a resist-coated substrate.

72. The method according to claim 62, wherein said carbon dioxide is supercritical carbon dioxide.

73. The method according to claim 62, wherein said cleaning adjunct comprises an acid.

74. The method according to claim 62, wherein said cleaning adjunct comprises a base.

75. The method according to claim 62, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

76. The method according to claim 62, wherein said cleaning composition is a liquid cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

77. The method according to claim 62, wherein said cleaning composition is a supercritical cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical cleaning composition so that it is converted to a liquid cleaning composition.

78. The method according to claim 62, wherein said removing step is carried out by diluting said cleaning composition with additional carbon dioxide.

79. A method according to claim 62, wherein a said cleaning step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2 and then heated to produce a supercritical fluid, after which said supercritical fluid is removed while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

80. A method according to claim 62, wherein said cleaning comprises removal of water from said device.

81. The method according to claim 62, wherein said removing step is carried out while inhibiting redeposition of contaminants on said surface portion.

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82. A method of removing solid particulate contaminants from a microelectronic device, comprising the steps of:

providing a substrate having a surface portion to be cleaned of solid particulates therefrom,

providing a densified carbon dioxide cleaning composition, said cleaning composition comprising carbon dioxide and a cleaning adjunct, said cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

immersing said surface portion in said densified carbon dioxide cleaning composition for a time sufficient to remove at least a portion of said solid particulates from said surface portion; and then

removing said cleaning composition from said surface portion.

83. The method according to claim 82, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said secondary gas.

84. The method according to claim 82, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing clean heated supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said heated supercritical CO_2.

85. The method according to claim 82, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said liquid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said secondary gas.

86. The method according to claim 82, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing clean heated gas or supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said heated gas or supercritical CO_2.

87. The method according to claim 82, wherein said densified cleaning composition is a liquid and is at saturated vapor pressure, and said removing step is carried out by draining said liquid with vapor side communication between said cleaning chamber and a receiving vessel.

88. The method according to claim 82, further comprising:

maintaining said cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step.

89. The method according to claim 82, wherein said microelectronic device comprises a microelectromechanical device.

90. The method according to claim 82, wherein said microelectronic device comprises an optoelectronic device.

91. The method according to claim 82, wherein said microelectronic device comprises a resist-coated substrate.

92. The method according to claim 82, wherein said carbon dioxide is supercritical carbon dioxide.

93. The method according to claim 82, wherein said cleaning adjunct comprises a co-solvent.

94. The method according to claim 82, wherein said cleaning adjunct comprises a surfactant.

95. The method according to claim 82, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

96. The method according to claim 82, wherein said cleaning composition is a liquid cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

97. The method according to claim 82, wherein said cleaning composition is a supercritical cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical cleaning composition so that it is converted to a liquid cleaning composition.

98. The method according to claim 82, wherein said removing step is carried out by diluting said cleaning composition with additional carbon dioxide.

99. A method according to claim 82, wherein a said cleaning step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2 and then heated to produce a supercritical fluid, after which said supercritical fluid is removed while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

100. A method according to claim 82, wherein said cleaning comprises removal of water from said device.

101. A method according to claim 82, wherein said removing step is carried out while inhibiting redeposition of contaminants on said surface portion.

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102. A method of cleaning contaminants from a microelectronic device, comprising the steps of:

providing a substrate having a surface portion to be cleaned,

providing a densified carbon dioxide cleaning composition, said cleaning composition comprising carbon dioxide and a cleaning adjunct, said cleaning adjunct selected from the group consisting of cosolvents, surfactants, and combinations thereof;

immersing said surface portion in said densified carbon dioxide cleaning composition; and then

removing said cleaning composition from said surface portion; while inhibiting redeposition of contaminants on said surface portion.

103. The method according to claim 102, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said secondary gas.

104. The method according to claim 102, wherein said densified carbon dioxide cleaning composition is a supercritical fluid, and said inhibiting step is carried out by:

introducing clean heated supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said supercritical fluid from said surface portion under pressure from said heated supercritical CO_2.

105. The method according to claim 102, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing a clean secondary gas into said liquid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said secondary gas.

106. The method according to claim 102, wherein said densified carbon dioxide cleaning composition is a liquid, and said inhibiting step is carried out by:

introducing clean heated gas or supercritical CO_2 into said supercritical fluid cleaning composition; and

removing said liquid cleaning composition from said surface portion under pressure from said heated gas or supercritical CO_2.

107. The method according to claim 102, wherein said densified cleaning composition is a liquid and is at saturated vapor pressure, and said removing step is carried out by draining said liquid with vapor side communication between said cleaning chamber and a receiving vessel.

108. The method according to claim 102, further comprising:

maintaining said cleaning composition as a homogeneous composition during at least one of said immersing step and said removing step.

109. The method according to claim 102, wherein said microelectronic device comprises a microelectromechanical device.

110. The method according to claim 102, wherein said microelectronic device comprises an optoelectronic device.

111. The method according to claim 102, wherein said microelectronic device comprises a resist-coated substrate.

112. The method according to claim 102, wherein said carbon dioxide is supercritical carbon dioxide.

113. The method according to claim 102, wherein said cleaning adjunct comprises a co-solvent.

114. The method according to claim 102, wherein said cleaning adjunct comprises a surfactant.

115. The method according to claim 102, wherein said providing step is carried out by mixing said carbon dioxide with said adjunct to produce a homogeneous solution.

116. The method according to claim 102, wherein said cleaning composition is a liquid cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by pressurizing said enclosed chamber with a second compressed gas by an amount sufficient to inhibit boiling of said drying composition.

117. The method according to claim 102, wherein said cleaning composition is a supercritical cleaning composition, wherein said immersing and removing steps are carried out in an enclosed chamber, and wherein said removing step is carried out by adding a second material to said supercritical cleaning composition so that it is converted to a liquid cleaning composition.

118. The method according to claim 102, wherein said removing step is carried out by diluting said cleaning composition with additional carbon dioxide.

119. A method according to claim 102, wherein a said cleaning step is initiated with said drying composition in a liquid state, and after a period of time said composition is diluted with pure liquid CO_2 and then heated to produce a supercritical fluid, after which said supercritical fluid is removed while maintaining the temperature of the fluid and gas above the critical temperature of CO_2.

120. A method according to claim 102, wherein said cleaning comprises removal of water from said device.

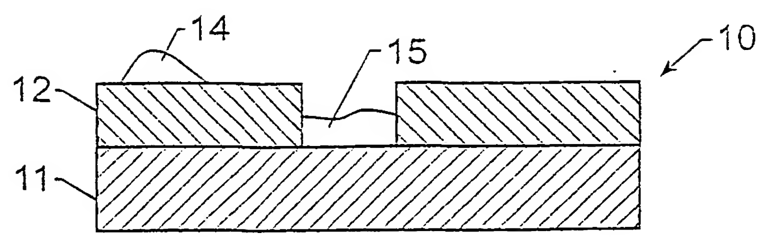

FIGURE 1

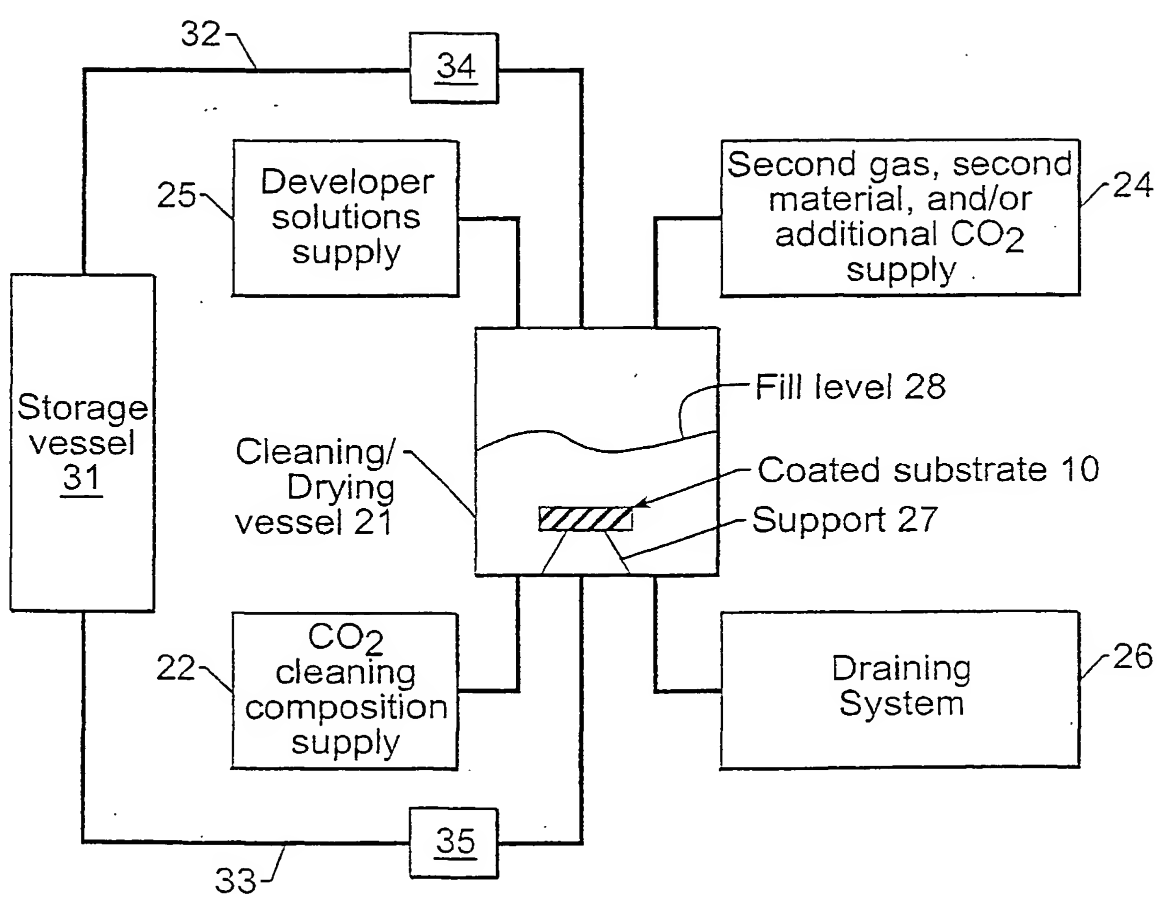

FIGURE 2

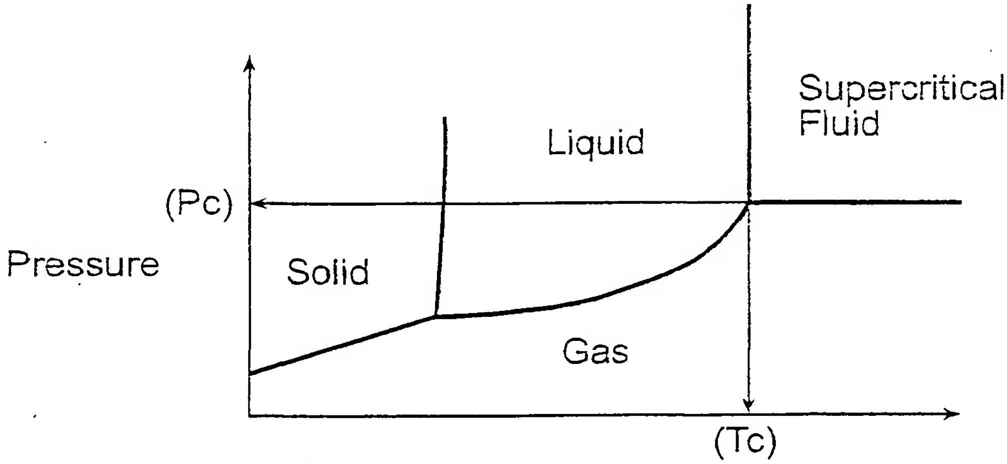

FIGURE 3

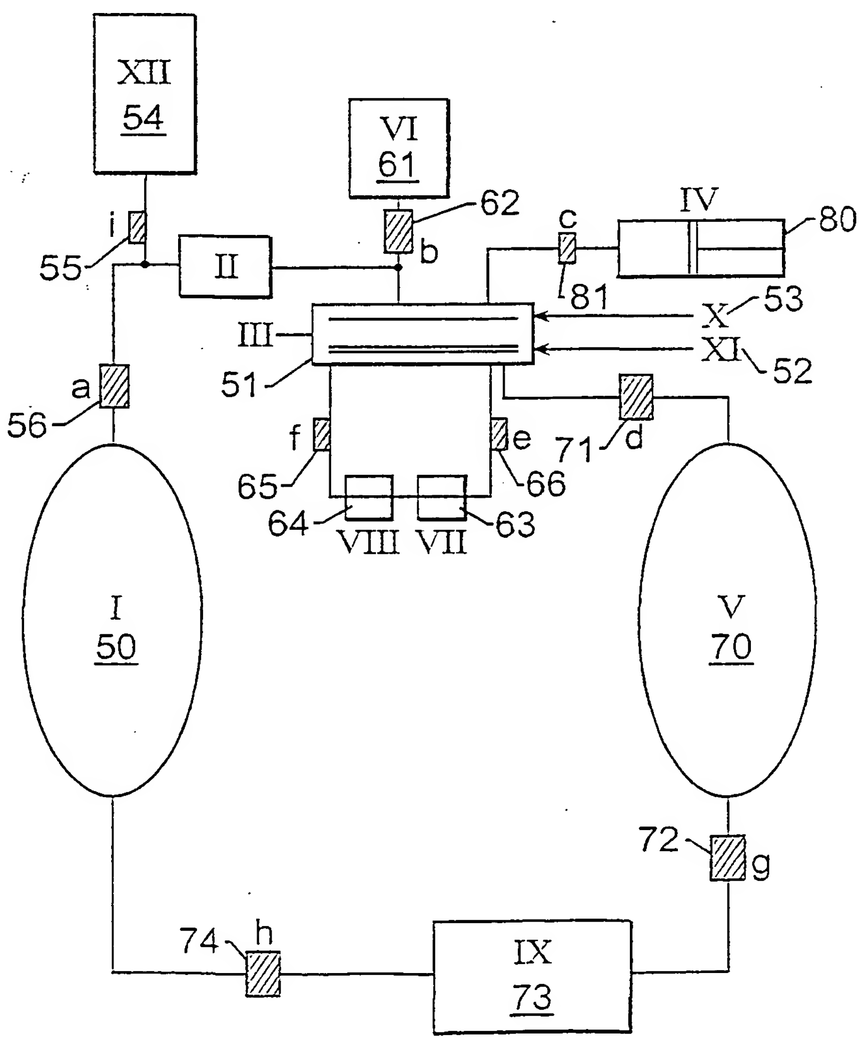

FIGURE 4

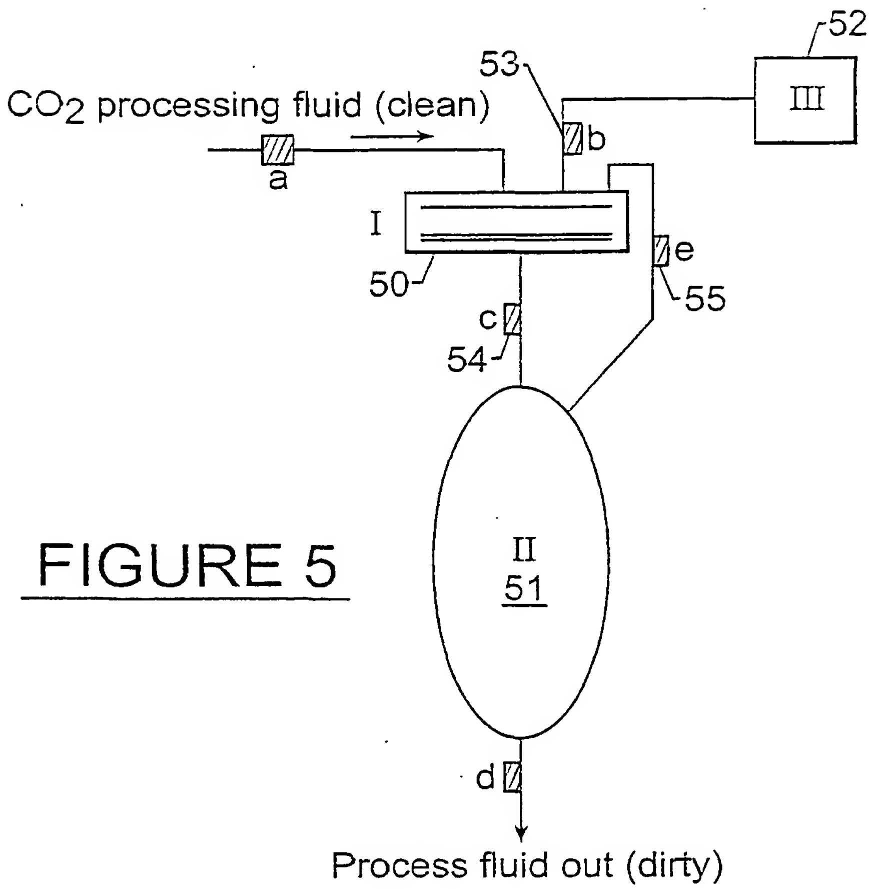
CO2 processing fluid (clean)
a
b
53
52
III
I
50
e
55
c
54
II
51
d
Process fluid out (dirty)

FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/04398

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : B08B 3/00; F26B 3/00; G03F 7/42; H01L 21/00
US CL : 134/2.902; 438/906; 34/402,404
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 134/1,1.3,2.3,30,34,36,37,42902; 438/906; 34/402,404

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P --- Y,P	US 6,306,564 B1 (MULLEE) 23 October 2001 (25.10.01), column 2, line 16 - column 5, line 9).	1-20,43-120 --- 21-42
X,P — Y,P	US 6,277,753 B1 (MULLEE et al) 21 August 2001 (21.08.01), column 2, line 13 - column 54.	1-20, 43-120 --- 21-42
Y,P	US 6,242,165 B1 (VAARTSTRA) 5 June 2001 (05.06.01), column 3, lines 18-25).	14,15,36,37
Y	US 5,783,082 A (DESIMONE et al) 21 July 1998 (21.07.98), column 2, line 25 - column 5, line 51.	8-10,30-32
Y	"Supercritical CO2 Process Offers Less Mess From Semiconductor Plants," Chemical Engineering Magazine, pp.27 and 29, Jul 1998 ed.	1-120
Y	Hideo Namatsu, "Supercritical Drying for Water-Rinsed Resist Systems," J. Vac. Sci. Technol. B 18(6) Nov/Dec 2000, pp. 3308-3312.	1-120
Y	Steven T. Walsh, "Overcoming Stiction in MEMS Manufacture," Micro, March 1995, pp. 49-58.	1-120

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 14 June 2002 (14.06.2002)	Date of mailing of the international search report 22 JUL 2002
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Randy P. Gulakowski Telephone No. (703)308-0661

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	W. Dale Spall, "Supercritical Carbon Dioxide Precision Cleaning for Solvent and Waste Reduction," International Journal of Environmentally Conscious design & Manufacturing, Vol. 2, No. 1, pp. 81-86, 1993.	1-120
A	US 6,067,728 A (FARMER et al) 30 May 2000 (30.05.00), abstract.	1-120
A	US 6,024,801 A (WALLACE et al) 15 February 2000 (15.02.00), column 1, lines 20-25, 34-36; column 3, lines 21-55); column 5, lines 19-21.	1-120